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A Study on Reactive Ion Etching of Barium Strontium Titanate Films Using Mixtures of Argon (Ar), Carbon Tetrafluoride (CF_4), and Sulfur Hexafluoride (SF_6)

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14. ABSTRACT
Barium Strontium Titanate (BST) is a complex oxide material with ferroic properties which has been considered for applications ranging from non-volatile memory to microwave tunable devices. When grown in bulk films BST forms a continuum of domains. It is theorized however, that when the material can be grown on the order of a single domain, its properties will drastically change. To exploit the ferroic properties of BST we developed a device fabrication method utilizing self-aligned etching to create metal-insulator-metal (MIM) varactors. As part of this method we employed reactive ion etching (RIE) to remove BST and create cylindrical island stacks consisting of platinum top electrodes, atop a layer of BST, atop a platinum bottom electrode film, all on top of a sapphire substrate. Here we report and compare the results of a study on using RIE to remove BST using combinations of three gas, argon (Ar), carbon tetrafluoride (CF_4), and sulfur hexafluroride (SF_6).

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reactive ion etching, barium strontium titanate, argon, carbon tetrafluoride, sulfur hexafluoride

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1. Introduction and Background

Barium strontium titanate (BST) is a complex oxide material with ferroic properties that has been considered for applications ranging from nonvolatile memory to microwave tunable devices.[1] Ferroic materials fall into four primary orders that include ferroelectricity, ferromagnetism, ferroelasticity, and ferrotoroidicity (which has not yet been observed). A material that exhibits two or more of these properties is known as a multiferroic. When grown in bulk or as thick films these materials form a continuum of individual domains. It is theorized, however, that if these materials can be structured with physical dimensions on the order of the size of a single domain, their ferroic properties will drastically change.[2,3] For a collection of nanoparticles with radii smaller than a magnetic exchange length an effect known as superparamagnetism is predicted.[4]

In order to exploit the properties of ferroic thin film materials these materials must be configured into device structures. One of the most critical post growth process science methods used to construct practical device structures is dry etching. Dry etching, namely reactive ion etching (RIE), of the ferroic thin film material enables the pattern delineation to create the device structure. A novel method to create micro/nano structures is the self-aligned RIE technique. This study investigates and develops the self-aligned RIE technique to create small-scale BST device structures. This method utilizes traditional photolithography techniques and RIE to create metal-insulator-metal (MIM) varactors. Typically, dry etching techniques use a radio frequency (RF) power supply to place a high-frequency voltage difference between two parallel metal plates on a chamber held at low vacuum. Argon (Ar) gas is used to physically bombard the material to be etched. RIE introduces an additional gas or gases, that when broken down, generate reactive ions that also chemically attack the material to be etched. In this report, Ar is used in various concentrations with carbon tetrafluoride (CF_4) and sulfur hexafluoride (SF_6) to construct MIM varactors, made of Pt/BST/Pt* on sapphire substrates, using RIE.

[1] Kumar, A.; Manavalan, S. G. Characterization of Barium Strontium Titanate Thin Films for Tunable Microwave and DRAM Applications. *Surface & Coatings Tech* **1–3 August 2005,** *198,* 406–413.

[2] Kittel, C. *Phys. Rev.* **1946,** *70,* 965–971.

[3] Toonen, R.; Cole, M. Third-Order Electric-Field-Induced Dipolar Resonances From Patterned Barium-Strontium-Titanate Thin-Films. *App Phys Lett*. **2012,** *100,* 222908.

[4] Rüdiger A.; Schneller, T.; Roelofs, A.; Tiedke, S.; Schmitz, T.; Waser, R. Nanosize Ferroelectric Oxides – Tracking Down the Superparaelectric Limit. *Appl. Phys. A* **2005,** *80,* 12471255.

* Pt is platinum.

2. Experimental Procedure

Whole, 2-inch-diameter, 330-μm-thick, (0001) epi-ready sapphire wafers were sputter cleaned in Ar using a Lesker CMS18 sputter unit. Subsequent to the substrate cleaning, two layers of film were deposited. First, a layer of Pt was direct current (DC) sputter deposited to create a bottom electrode. Then, the ferroic film, a layer of $B_{60}S_{40}TiO_3$,* was RF sputter deposited over the Pt bottom electrode. Following the film depositions the wafer was cleaved into 1 × 1-cm-square test structures, whereby several samples were randomly selected for scanning electron microscopy (SEM) analyses to determine Pt and BST layer thicknesses. Pt layers ranged from 120 to 225 nm while BST layers ranged from 165 to 330 nm. The films themselves were very uniform over any given wafer. Hence, the wide variations reported here are due to differences from wafer to wafer.

To construct the MIM varactors the following photolithography steps were employed. First, a lift off resist, LOR 30B (MicroChem, Inc.), was spin coated at 2000 revolutions per minute (rpm) for 1 min. Next, samples were soft baked at 180 °C on a hot plate for 5 min. Then photoresist, SC-1827 (Shipley), was spin coated at 5500 rpm for 30 s followed by a hard bake at 95 °C for 30 min. Next, samples were exposed to 405-nm ultraviolet (UV) light for 18 s at 10 mW/cm2† using a mask-aligner in contact mode with a chrome mask. Samples were then developed in MF-319 developer for 105 s followed by a 15 s bath in deionized (Di) water and then a 105 s bath in Di water. Samples were dried with nitrogen (N_2) then placed into a sputter chamber for deposition of the Pt top electrode (TE) that will serve as the etch mask in the RIE process. The DC sputter deposition parameters were optimized to produce a TE thickness of approximately 160 nm. Finally, samples were soaked in Remover PG (MicroChem) at 55 °C overnight with subsequent removal of underlying lift-off-resist (LOR) revealing islands of circular, Pt TEs on BST.

Reactive ion etching was carried out using a March CS-1701 Reactive Ion Etcher. To supply power to the RIE a RFX-600 RF generator was used to deliver 500 W at 13.56 MHz with an output impedance of 50 ohms. The gases that were used were combinations of Ar and CF_4, and Ar and SF_6. Vacuum pressures within the March RIE were 200 mTorr with a total gas flow rate of 20 sccm‡. Etching times ranged from 4 to 30 min. Once etched samples were then cleaved in half and analyzed using a SEM to determine subsequent thickness of BST.

*Notation indicates that the percentage of B to S is 60:40. Also implied in this notation is that proportionally, B+S=T or (B+S):T.

† milliWatt per square centimeter.

‡Standard cubic centimeter per minute.

3. Results and Discussion

Samples were run in mixtures of $Ar:CF_4$ and $Ar:SF_6$ at concentrations of both 20:80 and 40:60. Results of these mixtures are plotted in figures 1 and 2 that compare etchant concentrations. Averaging the data yielded etching rates of 5.7 and 6.1 nm/min for $Ar:CF_4$ 20:80 and 40:60, respectively, and 7.5 and 8.0 nm/min for $Ar:SF_6$ 20:80 and 40:60, respectively. Immediately it shows that increasing the argon to chemical etchant ratio increases the etch rate slightly while switching from CF_4 to SF_6 increases the etch rate more significantly. In fact an initial etch of 180 nm of BST for 30 min with $Ar:SF_6$ at 20:80 found the film to be completely etched away. Hence, shorter etch times were necessary for $Ar:SF_6$.

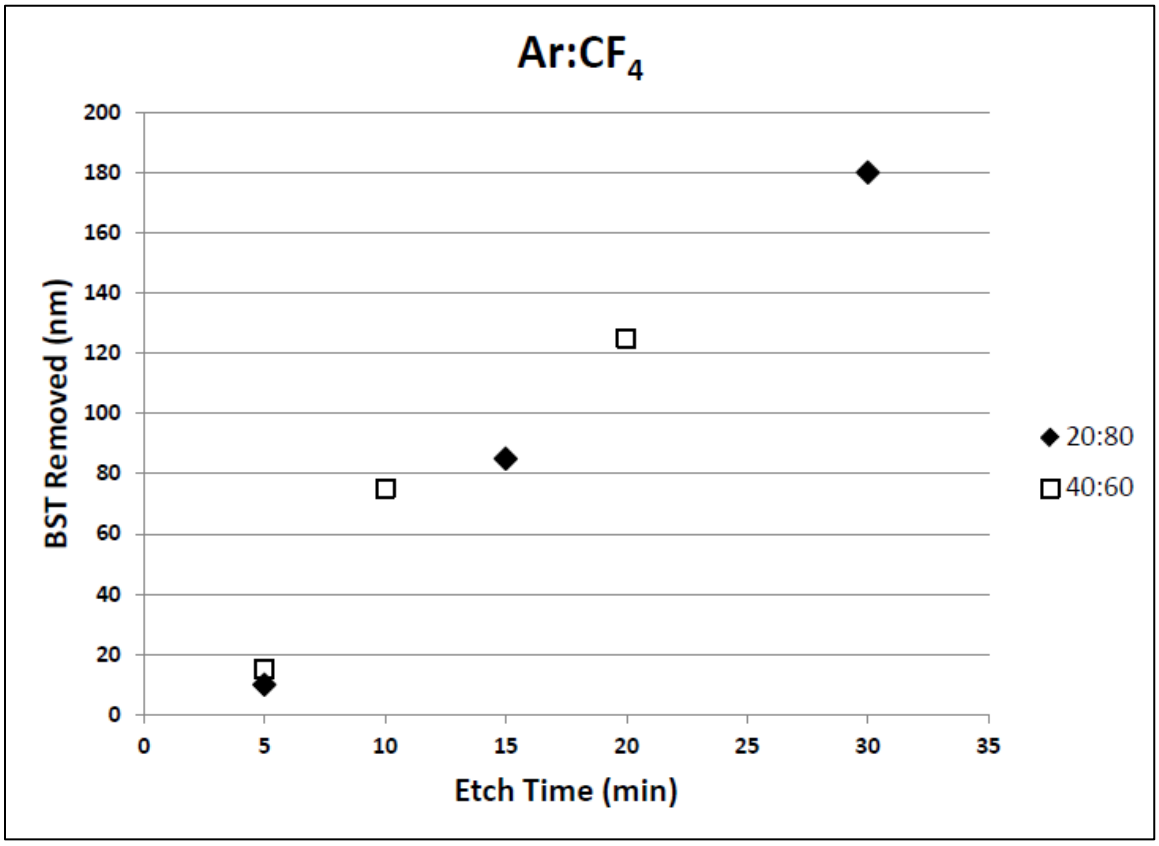

Figure 1. Amount of BST removed vs. etch time for $Ar:CF_4$.

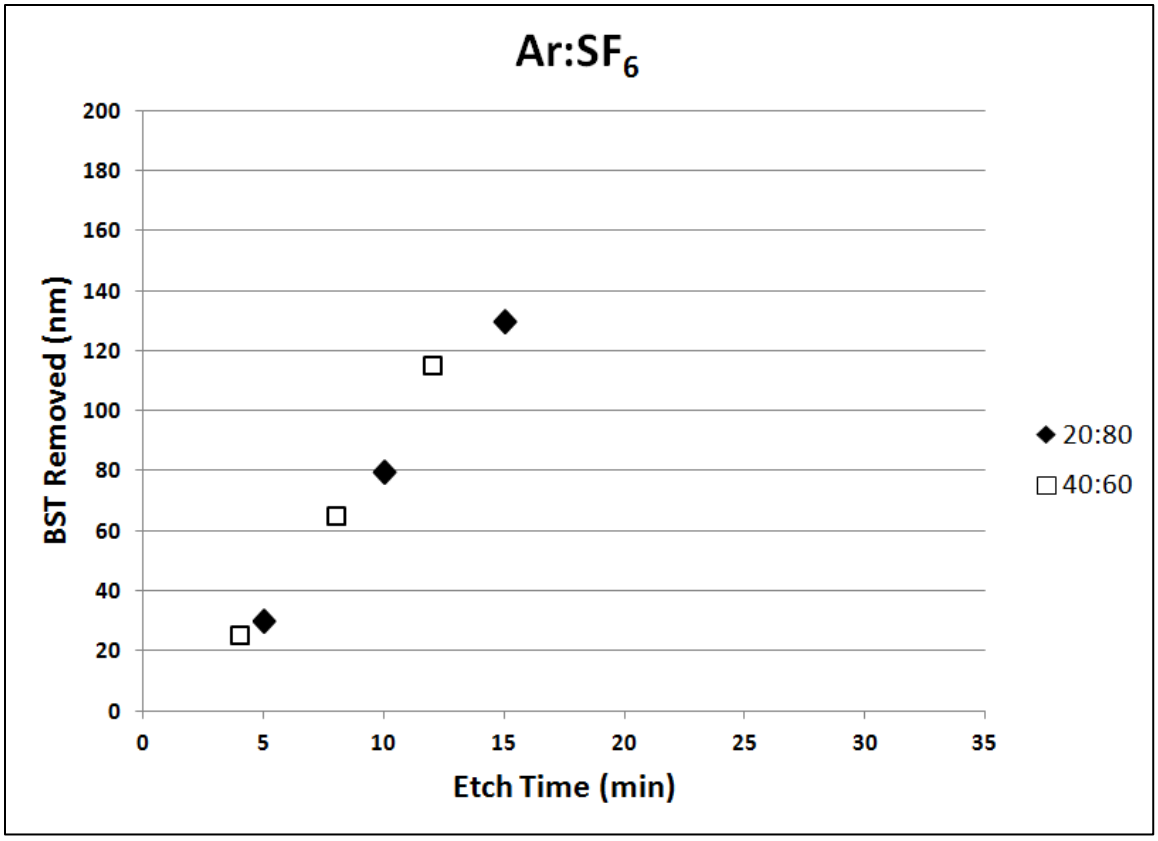

Figure 2. Amount of BST removed vs. etch time for $Ar:SF_6$.

Upon visual inspection most samples appeared to indicate that the etched films were very uniform as displayed by their evenness of color over their entire surface. Figure 3 is a SEM micrograph cross-section of a typical MIM varactor showing BST film sandwiched between two Pt electrode layers, is a good representation of this uniformity.

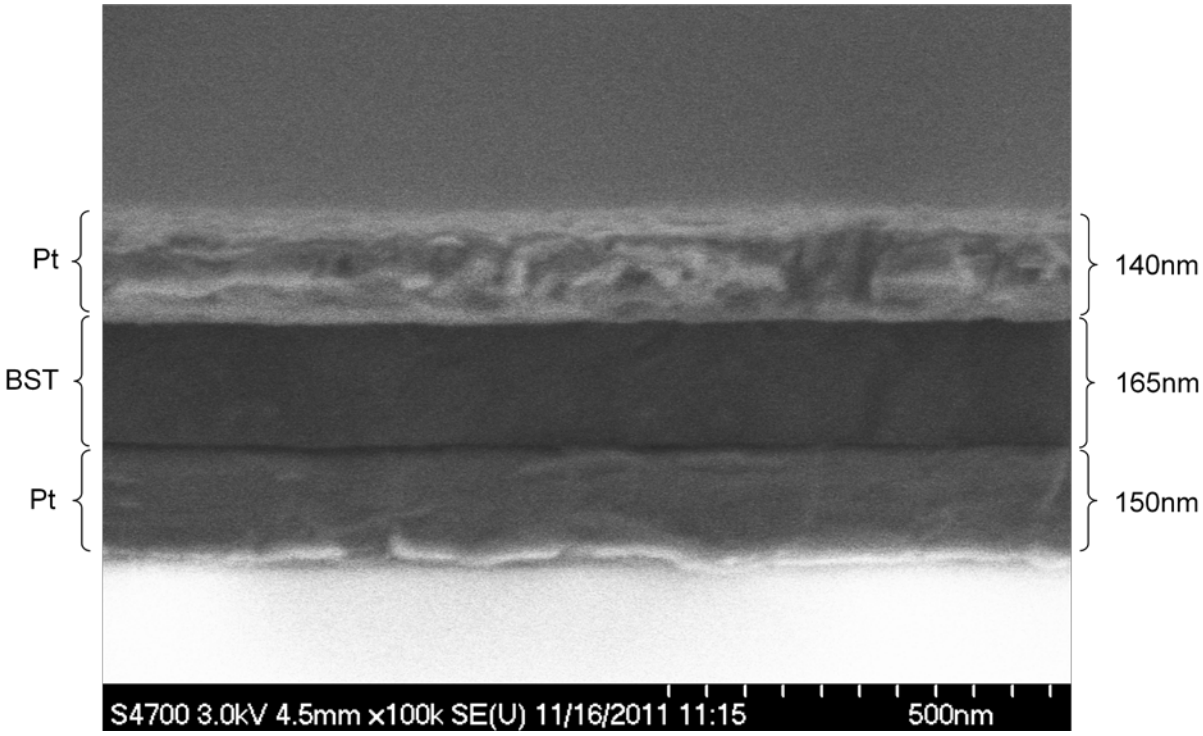

Figure 3. SEM cross-section of varactor showing the Pt bottom electrode, BST film, and Pt TE.

4. Conclusions

In an effort to develop a process science method to construct self-aligned MIM varactors, layers of Pt followed by a ferroic film, $B_{60}S_{40}TiO_3$, were first deposited on (0001) epi-ready sapphire substrates. The 1 × 1-cm samples were then cleaved and traditional photolithography was subsequently used to deposit circular, Pt TEs onto the BST. A dry etch process via RIE was then conducted using combinations of Ar:CF_4 and Ar:SF_6 at ratios of both 20:80 and 40:60. Etching rates were found to be 5.7 and 6.1 nm/min for Ar:CF_4 20:80 and 40:60, respectively, and 7.5 and 8.0 nm/min for Ar:SF_6 20:80 and 40:60, respectively. Etched samples were also of highly uniform thickness.

List of Symbols, Abbreviations, and Acronyms

Ar	argon
BST	barium strontium titanate
CF_4	carbon tetrafluoride
DC	direct current
Di	deionized
LOR	list-off-resist
MIM	metal-insulator-metal
mW/cm^2	milliWatt per square centimeter
N_2	nitrogen
Pt	platinum
RF	radio frequency
RIE	reactive ion etching
rpm	revolutions per minute
sccm	standard cubic centimeter per minute
SEM	scanning electron microscopy
SF_6	sulfur hexafluoride
TE	top electrode
UV	ultraviolet

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